



INFLUENCE OF SOLVENT AND ISOSBESTIC POINT ON A NOVEL PREPARED REAGENT COMPOUND 4-HNPBS DERIVED FROM SULPHADIAZINE

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Abstract

Different polar solvents have been used to record and analyze the electronic absorption spectra of 4-NHPBS (E)-4-((2-hydroxynaphthalen-1-yl)diazanyl)-N-(pyrimidin-2-yl)benzenesulfonamide. The coefficients of determination for regression and correlation were computed using multiple linear regression methods. The empirical Kamlet-Taft solvent parameters were used as a starting point for these regressions, based on an equation linking the absorption bands' wavenumber maxima (ν_{max}). Dipolarity/polarizability, hydrogen-bond donor acidity, and hydrogen-bond receptor basicity are all properties of solvents. This analysis's regression fits provide a means of assessing the relative contribution of different types of interaction to overall spectral changes in the solution. The resulting bands are impacted by both specific and non-specific solute-solvent interactions, as shown by the dependency of ν_{max} on the solvent parameters. The pKa and the isosbestic point of the reagent 4-HNPBS were determined using UV-Vis spectrophotometry. The alcoholic solution of 4-HNPBS was mixed with water in a ratio of 0.1:4.9 of absolute ethanol to water. This ratio does not alter the maximum absorption. It shows the pH effect on the 4-HNPBS in the range of 1.0 to 12, and 530 shows the isosbestic point for the 4-HNPBS. Depending on the medium's acidity, the absorbance-pH plot at certain wavelengths displays a Z-shape curve with two inflections corresponding to pKa1, pKa2, and pKa3.

Keywords: Kamlet-taft, isosbestic point, pKa, Z-shape.

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1. Introduction

Different solvents' solvation and/or dielectric constants affect the absorption values [1]. The chemical features of the electronic transitions and the excited state in a molecule are taken into account by analyzing the impact of the solvent on the electronic absorption spectra. The maximum absorption shifts, making it one of the simplest ways to recognize and identify such impacts. This is associated with differences in solute and solvent properties [2]. Due to their tiny size and difficulty quantifying accurately, solvent effects are sometimes difficult to comprehend. It is also due to the fact that the observed shifts result from a combination of several influences acting in concert to produce the maximum wave numbers observed [3].

The solvent effect on absorption spectra is qualitative and quantitative[4]. While the refractive index is a quantitative way to measure how solvents affect spectra, researchers have been looking for a more qualitative and complete way to describe the solvent effect in order to understand how the dipole polarization of the solute molecule and the hydrogen bonding effect causes the spectra to shift. Since the transition moment is stabilized by an actuation-induced dipole interaction with the solvent molecule, solvent polarizability causes the absorption maximum to shift to lower energy.

In addition, the frequency shift of the spectral bands from the vapor state to the solution may be related to the differing stabilization energies of the excited and ground states, depending on the different types of intermolecular interaction [5]. High-bond-moment functional groups are often included in H-bonds [6]. Non-polar scattering in non-polar solvents leads to identical solvation energies for the ground and excited states of the solute, with the solvent's primary determining factor being the refractive index.

Non-polar solutes in polar solvents were shown to experience the same problem. It was discovered, however, that the dipole moment of a polar solute is crucial to its behavior in either a non-polar or polar solvent. This was shown to be the case when the number of H-bonding molecules and the number of solvent cage molecules increased. The reaction process causes a change in maximum absorption from blue to red in the first case, and the opposite in the second case.

The accumulation of H-bonding forces in polar solvents is predicted. However, its exact nature and timing depend on a wide range of situations. The intensity of the charge in the dipole moment during electronic transitions depends on a number of factors, including the size of the solvent and solute molecules and the magnitude of the solvent's dipole moment [7]. There have been several attempts to offer observational single-solvent polarity characteristics that correlate with solvent-dependent data, and these attempts have had varying degrees of success. In present work also we studied an essential parameter that demonstrates the degree of ionization of molecules in solution at various pH levels is the acid dissociation constant (pKa) number. The interactions of acidic and basic groups control a variety of chemical, physical, and biological properties of natural and synthetic compounds. Because the pKa in such substances regulates a variety of metabolic processes, including transport across membranes, biology, pharmaceuticals, medicine, and a wide range of other scientific disciplines are all very interested in learning more about it.

2. Experiment

2.1. Instrumentation

The instruments used in the current research were:

- Double beam (UV-Vis) Spectrophotometer, Biochrom Libra S60 England
- Test scan Shimadzu FT-IR 8400 Series Japan
- Electrical sensitive balance AD Company, Limited, Dool, CE HR 200 Japan

- E163694, Germany-pH-meter, WTW, listed,
- Laboratory equipment, including beakers, pipettes, and volumetric flasks of different sizes.

2.2. Preparation of standard solutions

The solutions used in the current research were:

- 0.1M reagent stock solution

The reagent solution was prepared by dissolving 0.2027 g in 5 mL of absolute ethanol using a 5 mL volumetric vial.

- 1M sodium hydroxide solution (NaOH)

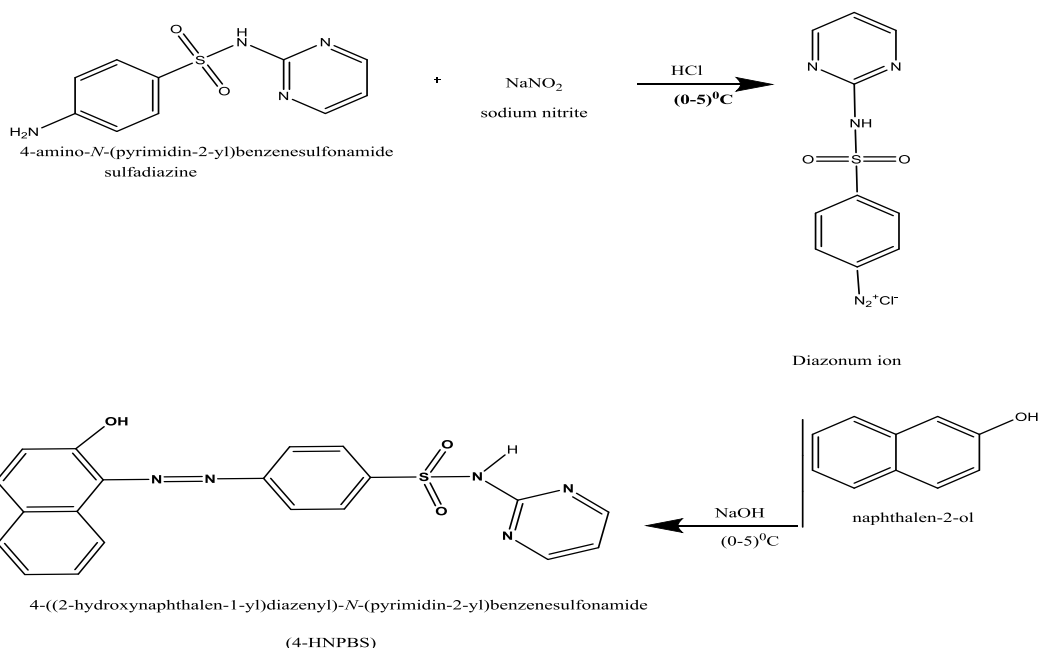
A sodium hydroxide solution was prepared by dissolving 2g of it in a small beaker and dissolving it in distilled water. The solution was transferred to a volumetric vial of 50 mL capacity, completing the volume to the mark.

- 1M of hydrochloric acid (HCl) solution

A 4.25 mL of concentrated hydrochloric acid was transferred to a volumetric vial of 50 mL capacity, and the volume was completed to the mark with DW.

2.3. Azo reagent (4-HNPBS)

Some studies have been carried out on the azo reagent (4-HNPBS). The azo reagent was previously prepared from the reaction of 2-naphthol pairs with the diazonium salt of sulphadiazine.



2.4. Azo Reagent (4-HNPBS) Studies

a- Effect of water volume

The prepared reagent solutions with 1×10^{-4} M concentrations of 1, 0.9, 0.8, 0.6, 0.4, 0.3, and 0.1 mL were diluted with DW to 4.0, 4.1, 4.2, 4.4, 4.6, 4.7, and 4.9 mL, respectively.

b- Effect of pH on reagents solution (4-HNPBS)

The 1×10^{-4} M reagent solution was prepared in 5 mL. A solution of 1M HCl was added to the first group and diluted NaOH (1M) was added to the second group to study the effect of pH in the range of 1.0 to 12. Scanned spectrophotometry from (180 to 800) nm was utilized against ethanol as a blank solution in the reference cell.

c- Dissociation constant of 4-HNPBS

The dissociation constant for the reagents was calculated in alkaline and acidic solutions. The solutions pH was adjusted with 1M HCl and 1M NaOH. Then, spectrophotometry was used to measure absorbance against pH using ethanol altered with determined volume of water as a blank solution in the reference cell. The Z-shaped plot between absorbance and pH shows the value of the dissociation constant.

d- Effect of organic solvents on (4-HNPBS)

The absorption spectrum of the synthesized organic reagents was recorded over a wavelength range of (180-800) nm in solvents of different polarities. Solvents such as methanol, acetone, DMSO, DMF, acetonitrile, 2-propanol, 2-butanol, 1,4-dioxane, and chloroform were used. Measurements were based on the dissolved a calculated amount to gave 0.0001M of organic compound. It was adjusted so that the absorption intensities were around 1.0. The measurements were performed at the lab temperature.

2. Results And Discussion

UV-Visible technique-

The reddish-orange solution for 4-HNPBS dissolved in ethanol showed peaks at 477 nm assigned to the absorption of the -N=N- group, as displayed in Fig.(1). Such absorptions emphasized that compound band was not found in all reacting molecules.

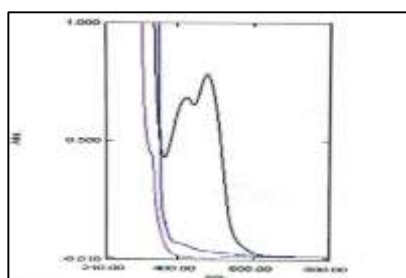


Fig (1): Absorption spectrum of 4-HNPBS in ethanol.

- Effect of organic solvents on (4-HNPBS)

The reagent of the present study was dissolved in absolute ethanol, and pH measurements of such non-aqueous solutions may result in some error since pH meter potential depends on the amount of H^+ ion present in the solution. Therefore, an alcoholic solution of 4-HNPBS was mixed with water in the ratio of 0.1:4.9 of absolute ethanol to water. This ratio did not alter the maximum absorption for each compound. Figure (2) shows the effect of pH on the 4-HNPBS range of 1.0-12, and 530 shows the isosbestic point for 4-HNPBS.

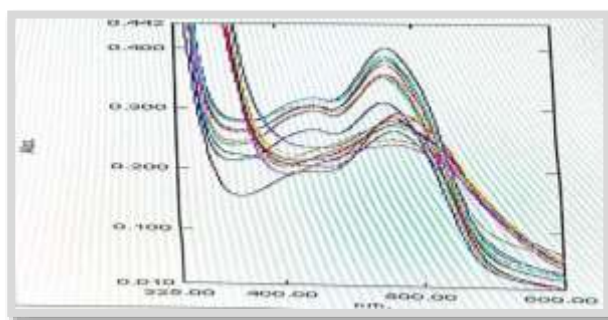


Fig (2): pH impact on 4-HNPBS for selected isosbestic spectra at 530nm.

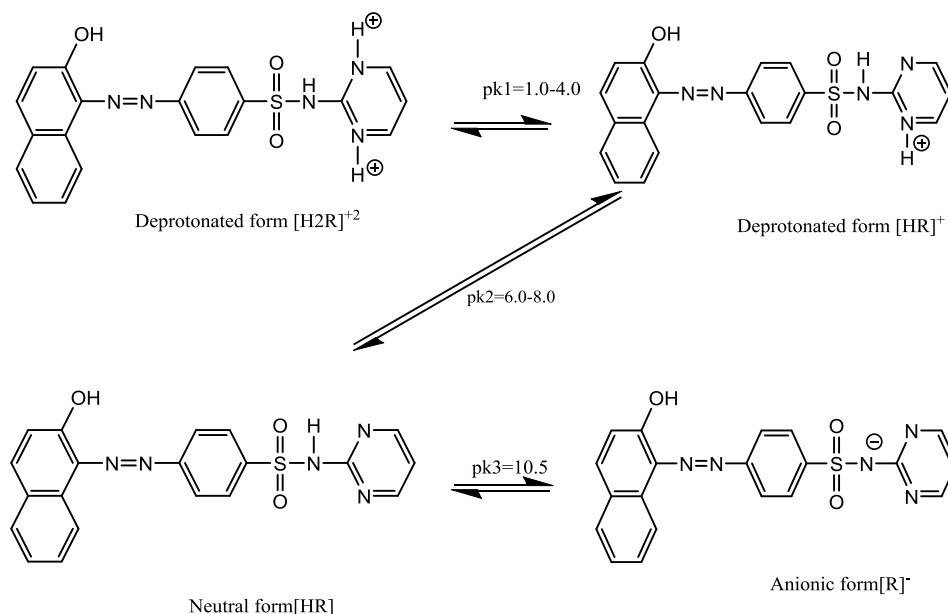


Fig.(3): Ionization forms of 4-HNPBS in acidic, neutral, and basic media.

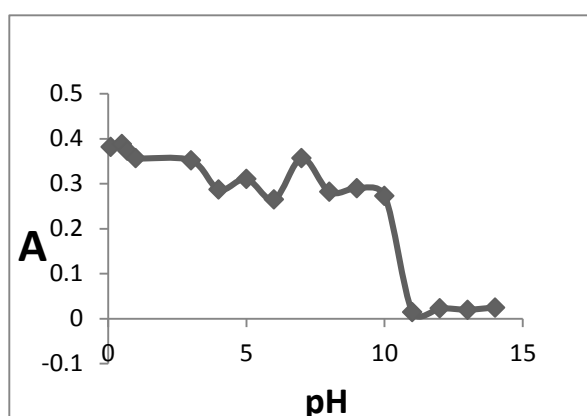


Fig.(4): The absorbance-pH plot of 4-HNPBS.

As can be seen in Fig. 3, the absorbance-pH plot at distinct wavelengths displays a z-shaped curve with two inflections. The medium's acidity determines whether these inflections are present. They were labeled pKa1, pKa2, and pKa3. Fig. 4 depicts the three different acid-base forms in a 4-HNPBS solution: LH^+ , LH^{+2} , and LH^- . Only in an acidic medium in a pH 1.0 can the completely protonated neutral species with the yellow hue of 479.5 and 482.5 nm be found. When the pH was between 4.0 and 6.0, the orange neutral predominated. Its highest absorption was seen between 482.5 and 483.5 nm for 4-HNPBS. As shown in Fig. (2), the spectra of the 4-HNPBS in the 10.5 medium reveal an absorption band with an isosbestic point located at 530 nm. This behavior explains why there is an equilibrium between the ionic and neutral forms of the substance [11,12].

Effect of water volume

When studying the effect of the water volume added to the reagent, the best peak was at 4.9 mL of the reagent with 0.1 mL distilled water, as shown in Fig. (5).

Table 1: Volums of reagent in exchange for the opposite sizes of DW.

D.W (mL)	0.1	0.3	0.4	0.6	0.8	0.9	1
Reagent (mL)	4.9	4.7	4.6	4.4	4.2	4.1	4
max λ	477.00	480.00	480.00	480.50	480.00	481.00	482.50
Abs	0.462	0.399	0.386	0.393	0.331	0.389	0.369

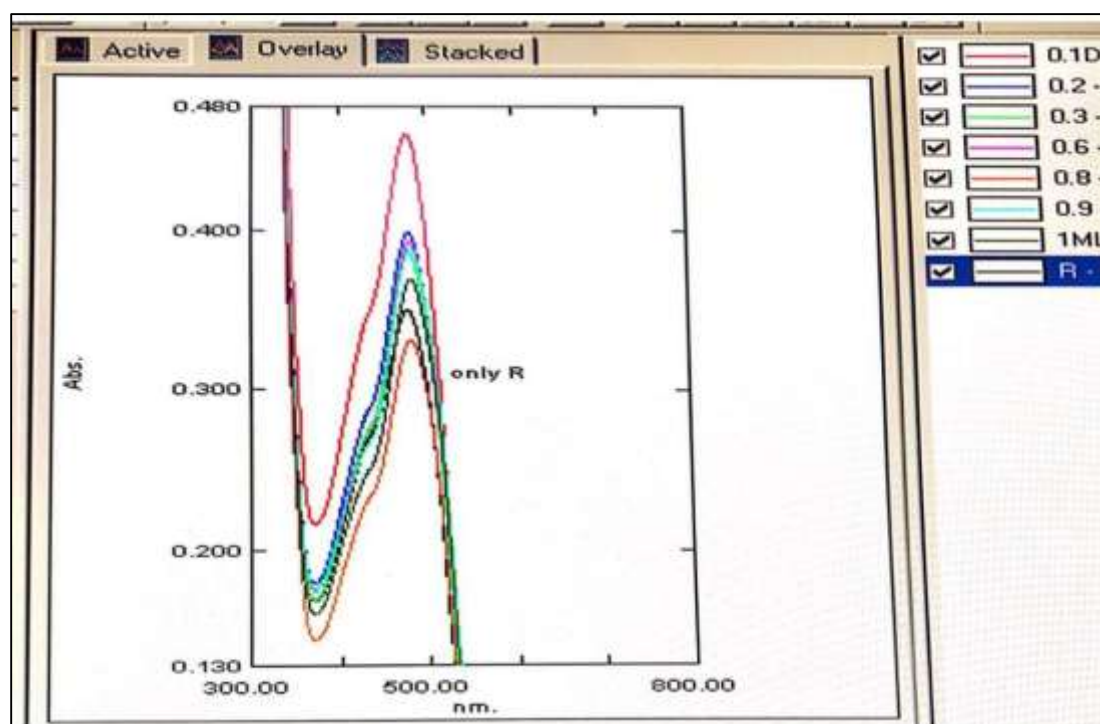
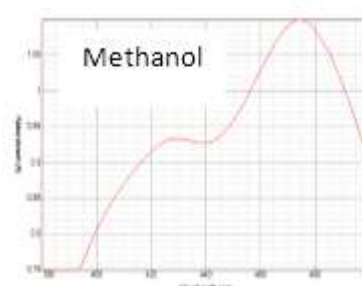
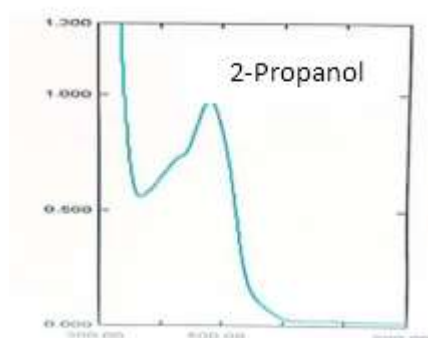


Fig.(5): The effect of the volume of water added to the 4-HNPBS

Solvent effect

Figures 6-13 display the results of scanning the absorption spectra of the investigated azo compounds in various solvents of varying polarities. These solvents include the protic solvents acetone, methanol, 2-propanol, and 2-butanol, and the aprotic solvents acetonitrile, 1,4-dioxane, dimethyl formamide, and chloroform.



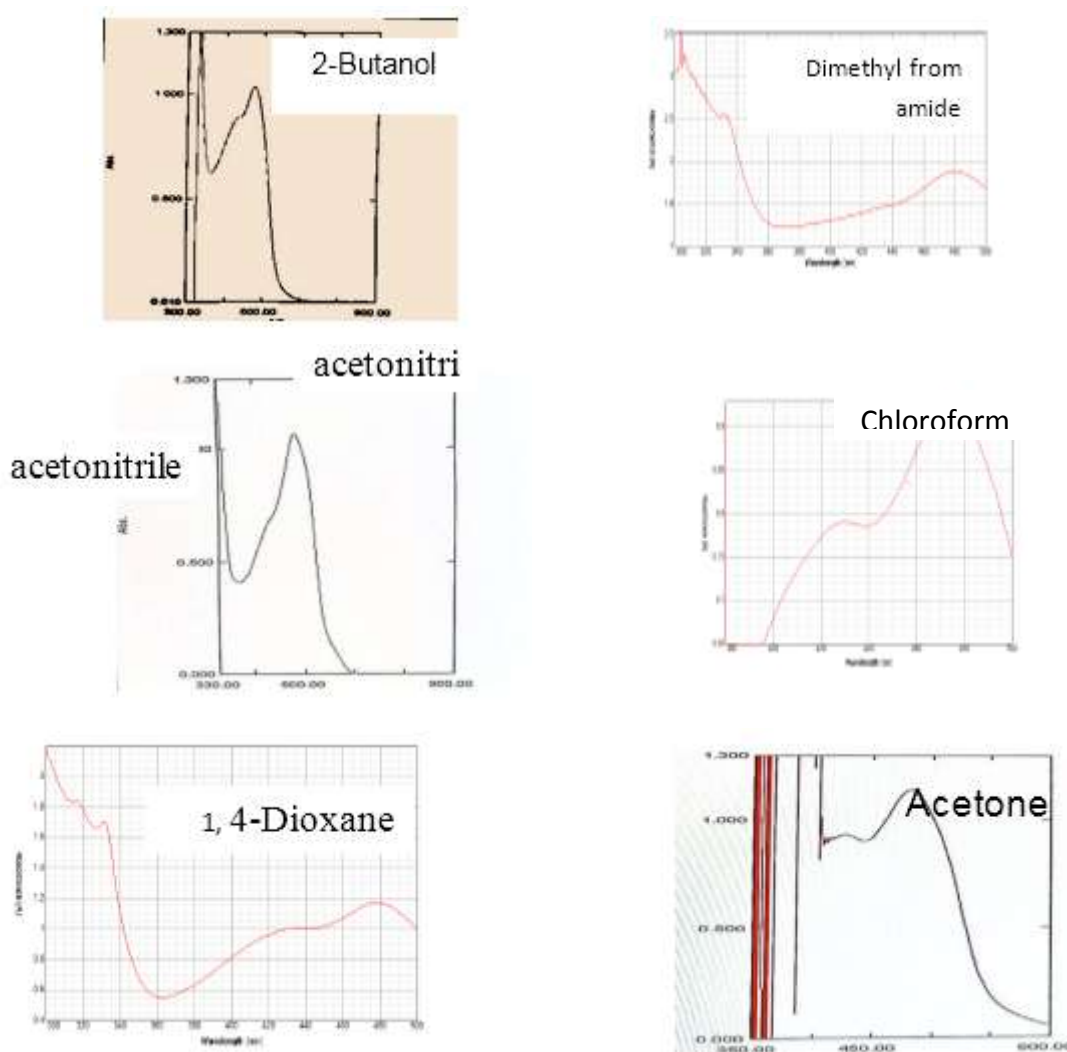


Fig. (6-13): Measured spectra of 4-HNPBS in the preferred solvents.

The electronic spectra's response to various solvents was measured. All forms of media include a unique mix of phenomena. The dielectric constant of a solvent is used in idealized theories as a quantitative indicator of the solvent's polarity [8, 9]. Hydrogen bonding and electron pair donor/electron pair acceptor (EPD/EPA) interactions are two examples of important solute-solvent interactions overlooked in this perspective.

Referring once again to the previously established definition of solvent polarity, it is evident from Figs. 13 and 14 that a single physical quantity cannot represent such a solvent dielectric constant in 4-HNPBS due to the fluctuation of λ_{max} as a function of the solvent dielectric constant. Solvent polarity is quantified on a multi-parameter scale known as the linear solvation energy relationship (LSER), which Kamlet and Taft introduced. Solvation effects entail significant interactions between a solute and its surroundings, and this method is commonly recognized as efficient and ambitious for researching these consequences. Calculating a compound's potential to create hydrogen bonds is another use of LSER. In solvatochromism, the Kamlet-Taft equation is represented by the following formula:^[10]

$$\nu^\circ = \nu + s\pi^* + b\beta + \alpha a \dots\dots\dots(1)$$

Where:

n = solvent's dipolarity/polarizability index,

β = hydrogen-bonding acceptor (HBA) of solvent basicity,

ν° = solute's regression value in cyclohexane as the reference solvent, and

a = measure of the solvent hydrogen-bonding donor (HBD) acidity.

The relative susceptibilities of the absorption frequencies with respect to the stated solvent variables are quantified by the regression coefficients b , s , and a in Equation (1).

Table 2 [11] presents the parameters of the solvent. The spectroscopic data correlations were achieved through the utilization of multiple linear regression analysis. The present study reports a positive correlation between the "B" and "a" parameters and the absorption frequencies of reagent compounds in various solvents. Table 2 presents the outcomes of the multiple regression analyses, including the coefficients ν° , s , b , and a . The efficacy of Equation (1) is demonstrated in Figures 14 and 15, wherein the absorption wavenumbers (ν_{calc}) obtained through computation are plotted against the associated theoretical values.

As the solvent hydrogen bond acceptor basicities increase, a bathochromic shift is shown by the negative sign of the "b" coefficient for the produced azo compounds in protic solvents. The observed rise in value suggests stabilizing the electronically excited state compared to the ground state. The positive signs of the "a" and "s" coefficients indicate the hypsochromic shift, corresponding to an increase in solvent polarity/polarizability and solvent hydrogen bond donor acidities. This proposal suggests stabilizing the ground state compared to the electronically excited state.

For 4-HNPBS compounds in both protic and aprotic solvents, the negative sign of "b" and coefficients indicates a bathochromic shift when the basicity of the solvent hydrogen bond acceptor increases and the acidity of the solvent hydrogen bond donor increases. The approach calls for maintaining a more stable electrically stimulated state than the ground one. Increasing solvent dipolarity/polarizability causes a hypochromic shift, as shown by the coefficient's positive sign. When compared to the electrically stimulated state, this suggests that the ground state is more stable.

Coefficients with a negative sign suggest bathochromic shifts when the dipolarity or polarizability of an aprotic case-solvent increases. The electrically excited state is also predicted to become more stable as a result of this. The negative sign of b and coefficients indicate that 4-HNPBS compounds in protic and aprotic solvents undergo a bathochromic shift with increasing basicity of the solvent hydrogen bond acceptor and acidity of the solvent hydrogen bond donor. This hypothesized that the electrically excited state could be stabilized concerning the ground state. Coefficients with a negative sign indicate bathochromic shifts when the dipolarity or polarizability of an aprotic case-solvent increase. This also suggests that the electrically excited state may be stabilized compared to the ground state [12].

Table(2): Selective Taft solvent characteristics (ϵ : dielectric constant) and azo compound absorption maxima in different solvents for 4-HNPBS.

Solvents	$\max\lambda$	ν°	$*\pi$	β	a	ϵ
Aceton	474.00	210970	0.62	0.48	0.08	20.7
Methanol	478.00	209205	0.6	0.63	0.93	32.6
2-Propanol	479.00	208768	0.48	0.84	0.76	19.92
2-Butanol	481.00	207900	0.4	0.80	0.69	16.56
Chloroform	482.00	207469	0.53	0.10	0.2	4.81
1,4-Dioxane	478.00	209205	0.62	0.480	0.0	2.3

Dimethyl amide	from	480.00	208333	0.88	0.69	0.0	7.6
Acetonitril		475.00	210526	0.66	0.40	0.19	37.5

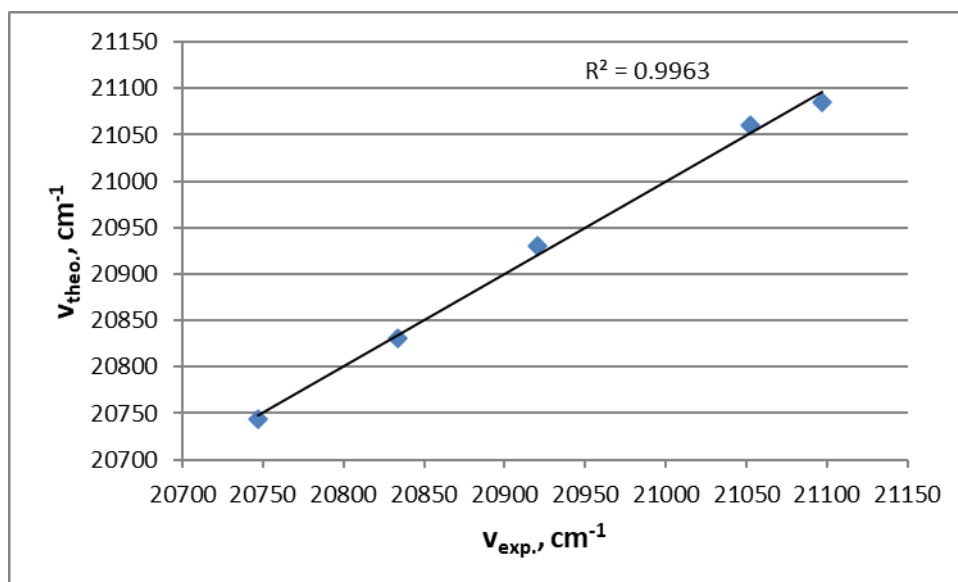


Fig.(14): The relation of the observed and calculated λ_{max} from Equation1 for 4-HNPBS in different protic solvents.

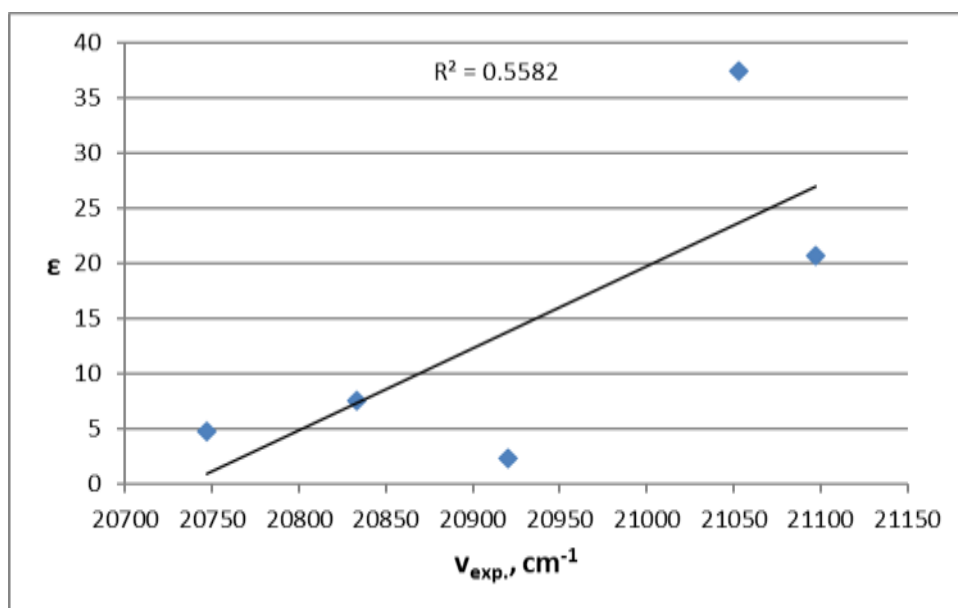


Fig.(15): The relation of the observed and calculated λ_{max} from Equation1 for 4-HNPBS in different aprotic solvents

3. Conclusion

When the absorbance vs pH plot was drawn, the isosbestic point emerged at 530 nm and had a Z shape. The characteristics of the solvents used modify 4-HNPBS's electronic spectra. Non-polar and polar solvent solvatochromic parameters of Eq. 1 agree with the electronic

spectral data (ν_{\max}) of 4-HNPBS, demonstrating the effective use of a linear solvation-free energy connection. It was shown that the three-parameter solvatochromic equation π^* . Hydrogen bonding types and the solvent dipolarity/polarizability impact may be evaluated using a and b . The electronic spectral data of 4-HNPBS has a weak association with the dielectric constants of the different solvents. It exemplifies that a single physical feature of solvent polarity cannot capture all intermolecular interactions between solute and solvent molecules.

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4. References

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